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LOW-MELTING GLAZE FOR STRUCTURAL CERAMICS

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A formula for a low-melting non-fritted glaze on the basis of a silicon-bearing rock (diatomite) and the technology for depositing this glaze on structural ceramics are developed. The elimination of the glaze melt fritting process allows for substantial savings in energy consumption.

A fairly great amount of attention in various countries has been paid to the surface treatment of bricks. In the past decades, little attention was paid in our country to imparting various color shades or special textures to bricks. However, under the current conditions of the market economy these issues have become important, and, consequently, new materials are required for technological processes.

A topical issue is the development of low-melting glazes, which do not require substantial energy consumption. The known fritted glazes are expensive and scarce. A study of amorphous silica, which is abundant in the Povolzhie territory, proved its suitability as the main component in the production of non-fritted glaze.

Amorphous silica is the opal rock containing 20 to 40% argillaceous material, and its content of active silica ranges from 25 to 50%. Amorphous silica has greater free surface energy than crystalline quartz and with much greater facility reacts with additives. Its use in the glaze composition makes it possible to exclude from the process such energy-consuming operations as high-temperature glaze melting and protracted milling of raw material, since natural amorphous silica, as a rule, is a finely disperse material.

The main shortcoming of amorphous silica used as the main raw material in the production of raw low-melting glazes is its high firing temperature (1200 – 1300°C), whereas the firing temperature of the traditional ceramic material is 900 – 1000°C. In view of this fact, we carried out an investigation involving the selection of components decreasing the temperature of raw glaze casting, coordination of the TCLE of ceramic crock and the resulting glaze, and the wetting capacity of glazes.

The raw material selected for the production of low-melting glazes was diatomite (amorphous silica), and the flux decreasing the casting temperature was borax $Na_2B_4O_7 \cdot 10H_2O$ (RF Patent No. 2070185).

The diatomite from the Zabaluiskoe deposit (Ulyanovsk Region) is amorphous silica, which is lightweight, porous, sometimes loosely structured and slightly argillaceous, with a molding moisture of 48.1 – 50.6%, fire resistance of 1500°C, and water absorption of 44.3 – 66.7%.

One of the advantages of diatomite is the possibility of its homogenous mixing with borax. In doing so, the borax particles become enveloped by amorphous silica, which makes it possible to obtain high-quality glaze without fritting. The glaze-production technology is simplified, and a substantial amount of energy is saved.

The clays that were selected to investigate the reaction of glazes with ceramics crock were from the Begishevskoe deposit and from the Alekseevskii Brick Factory, whose chemical compositions correspond to the average chemical composition of low-melting clays in Tatarstan.

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TABLE 1

Material	Mass content, %								
	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	calcination loss
Begishevskoe deposit clay	61.00	14.00	5.80	6.30	2.50	1.65	1.75	7.00	–
Alekseevskii Factory clay	68.46	–	10.50	4.51	4.81	2.22	2.00	0.31	6.27
Diatomite	80.20	–	2.10	–	6.10	0.84	1.13	3.38	6.41
Borax	–	36.51	–	16.26	–	–	–	–	47.23

The clay from the Begishevskoe deposit is loam with the average content of the fractions below 0.01 mm equal to 54.7%, and that of the fractions above 0.01 mm — 54.3% on the average. The loam has increased drying sensitivity (1.56), its total shrinkage is 9.5 – 10.8%, and its water absorption is 10.3 – 13.9%.

The clay from the Alekseevskii factory is little sensitive to drying, its plasticity number is 9.48, and its water absorption 14.14%. The chemical composition of the clays and glaze components is shown in Table 1.

Five glaze compositions were prepared by mixing the initial components (diatomite : borax) in the following ratios (wt.%): 70 : 30, 60 : 40, 50 : 50, 40 : 60, and 30 : 70.

In the beginning, it was necessary to determine the optimum ratio of the raw-material components, based on the main requirements imposed on the glaze coatings. The TCLE of the glaze should correspond to the TCLE of the ceramic crock on which the glaze is deposited (the deviation should not exceed 10%).

The TCLE values were calculated according to the Winkelman and Schott [1] method based on the additive dependence of the TCLE of the glaze and the crock on their chemical compositions:

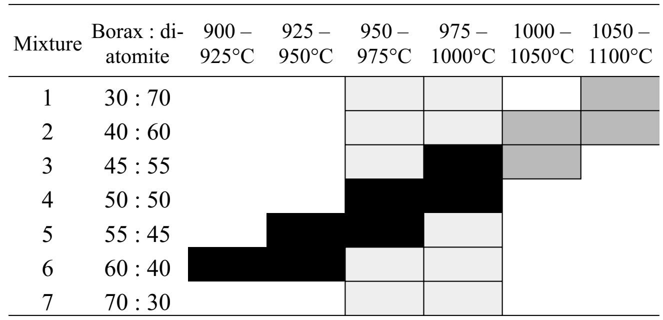
$$\alpha = \sum P_i x_i ,$$

where P_i is the weight content of oxides in glaze, %, and x_i are the empirical numerical factors characterizing the expansion of oxides or glaze.

The experimental determination of the TCLE was carried out using a DKV-5A quartz dilatometer. The TCLE of ceramic crock from the Begishevskoe deposit is about $6.8 \times 10^{-6}\ K^{-1}$, that of the Alekseevskii Factory clay $6.2 \times 10^{-6}\ K^{-1}$, and that of the glaze $6.5 \times 10^{-6}\ K^{-1}$, which is evidence of the coordination between the TCLE of the glaze and ceramics.

Non-fritted glazes were prepared by joint grinding of raw components (diatomite and borax) in a ball mill up to passing through a sieve with a cell size of 10,000 holes/cm^2. Next, an aqueous suspension of density 1.6 g/cm^3 was prepared and deposited on the ceramic surface.

In the ideal case, glass should be applied on a fired brick. However, in recent years, a tendency toward applying glaze to green brick has prevailed. In the course of firing, the glaze covers all defects in the brick, owing to its high fluidity. Non-fritted glaze as well can be deposited either on a dried green brick or on fired crock. If the glaze is deposited on a green brick, the glaze casting temperature should correspond to the firing temperature of the ceramic article. The casting of glaze on the surface of dried green brick is much more efficient.



Conventional symbols: ( ) dull glaze; ( ) lustrous glaze with bare spots (crock absorption); ( ) lustrous glaze with smooth surface.

Fig. 1. Diagram of the optimum glaze compositions depending on the casting temperature.

The temperatures of glaze casting were studied for different contents of the components. The optimal temperatures for glaze firing were determined, and the optimal compositions for this type of ceramics were selected. It can be seen from the diagram in Fig. 1 that the optimal firing temperature is 950 – 1000°C.

With the borax : diatomite component ratio equal to 60 : 40, the optimal temperature interval for casting was 900 – 950°C, and for the 50 : 50 ratio, it was 950 – 1000°C. When these mixtures and temperatures are used, the glaze has a smooth lustrous surface without crackle (microcracks). With the other ratios of the components, the glaze either has a dull surface or spreads with decreased viscosity when bare spots and, partly, crackle arise on the sample surface.

In order to obtain a range of colors in glaze coatings, it is recommended to introduce colorant agents into their compositions. The following compounds were selected: $Cu(OH)_2$, Cr_2O_3, $KMnO_4$, Fe_2O_3, and ZrO_2, which were introduced as additives (above 100%).

As a result of the performed studies, it was found that the introduction of colorant additives in the optimum ratios yields glazes of brown-green, green, and brown colors, as well as white opacified glazes.

REFERENCES

1. Yu. G. Duderov and I. G. Duderov, *Ceramic Technology Calculations* [in Russian], Stroiizdat, Moscow (1973).